Process for the separation and purification of an aqueous mixture comprising the main components acetic acid and formic acid

2. The PRIOR ART

The invention relates to a process for the separation and purification of an aqueous reaction mixture comprising the main components acetic acid and formic acid.

The preparation of acetic acid by catalytic oxidation of saturated and/or unsaturated hydrocarbons, for example the gas-phase oxidation of C_4-hydrocarbons, results in formation of product streams comprising as main components acetic acid, formic acid and water in varying proportions.

To work them up further, these product streams have to be separated into their individual components. Separation of a ternary acid/water mixture comprising acetic acid, formic acid and water into its pure components by distillation, for example, presents considerable problems since the system contains not only the binary water/formic acid maximum azeotrope but also a ternary water/formic acid/acetic acid saddle azeotrope.

If such a mixture has a high water concentration, separation by distillation has a tremendous additional energy requirement since all the water has to be distilled off at the top of a column as lowest-boiling component.

For the separation of aqueous mixtures having an acetic acid content of >60% by weight and a formic acid content of 5% by weight, Hunsmann and Simmrock (Chemie-Ing.-Tech., 38, 1966) recommend the use of azeotropic distillation for making the separation easier and for reducing the energy required. As azeotropic entrainer for the removal of water, ethyl n-butyl ether is proposed. The azeotrope of water and entrainer boils at about 91°C and contains about 10% by weight of water. The entrainer ethyl n-butyl ether forms no azeotrope with formic acid and acetic acid.

For separating off formic acid, DE-A 1204214 recommends azeotropic rectification using n-butyl chloride as entrainer. The disadvantage of this process is the use of chlorinated hydrocarbons as entrainer.

US-A 5633402 discloses a process for the separation of binary mixtures of formic acid and acetic acid by means of azeotropic distillation. Methyl formate is used as entrainer for the formic acid. Removal of water is not described in this process.

DE-A 4426132, EP-A 0635474, DE-A 19610356 (US-A 5662780) disclose various processes for the purification and dewatering of acetic acid by means of azeotropes with various entrainers. However, none of these processes describes the dewatering of a mixture of acetic acid and formic acid.

US-A 5173156, US-A 5006205, US-A 4877490 and
US-A 4935100 disclose processes for the dewatering of formic
acid by means of extractive rectification. Entrainers
mentioned here are, for example, cyclohexanone, oxalic acid,
decanoic acid and methyl salicylate.

EP-A 156309 (CA-A 1238919) and EP-A 12321
(US-A 4262140) describe the dewatering of formic acid by
extractive rectification using carboxamides as auxiliaries.
However, none of these processes describes the dewatering of
a mixture of acetic acid and formic acid.

The "Process Economics Program" Report No. 37A (1973)
of the Stanford Research Institute discloses a process for
the separation of an aqueous mixture comprising about 42% by
weight of acetic acid and 2% by weight of formic acid. In
this process, the aqueous mixture is concentrated by
countercurrent extraction with diisopropyl ether. In the
dewatering and solvent recovery column, the water is
distilled off at the top as an azeotrope of water and
diisopropyl ether. The bottom product, namely a mixture of
acetic acid and formic acid containing about 0.12% by weight
of water, is fractionated further by azeotropic
rectification. Benzene is used as entrainer for the formic
acid. A great disadvantage of this process is the low quality
of the formic acid separated off, which still contains about
1% by weight of acetic acid, about 2% by weight of water and

about 7% by weight of benzene. The use of benzene in this process and the residual benzene content in the formic acid make this process unattractive.

All the processes known from the prior art are either only suitable for satisfactorily separating binary mixtures such as acetic acid/water, formic acid/water and acetic acid/formic acid or only economically applicable to aqueous acid mixtures in which a high concentration of acid (>60% by weight) is present. Furthermore, some of the known processes are no longer acceptable from the point of view of today's safety and environmental standards because of their use of benzene or chlorinated hydrocarbons.

It is therefore an object of the invention to provide a process for the separation of a ternary, aqueous mixture of acids into its pure components, which process does not have the disadvantages mentioned in the discussion of the prior art.

It has now been found that the separation and purification of a mixture comprising the main components acetic acid, formic acid, water and high boilers (hereinafter referred to as crude acid) can be carried out particularly readily if the mixture is extracted by means of a solvent in a circulation process in a first step and the extract stream consisting predominantly of solvent, acetic acid, formic acid, high boilers and water is subsequently fractionated in

a sequence of distillation steps into the constituents

solvent which is recirculated to the extraction, water,

formic acid, acetic acid and high boilers, and the raffinate

stream is freed of solvent in a further distillation step by

means of a solvent stripping column.

The invention provides a process for the separation

and purification of an aqueous mixture comprising the main

components acetic acid, formic acid and high boilers by

extraction with a solvent in a circulation process, which

comprises feeding the raffinate stream containing a major

part of the water to a solvent stripping column (11) for

removal of the water and conveying the extract stream to a

solvent distillation column (8) from which, in a first step,

a mixture (A) comprising water and solvent is separated off

via the top and a mixture (B) comprising acetic acid, formic

acid and high boilers is separated off via the bottom,

separating the formic acid off from the mixture (B) in column

(29) and subsequently fractionating the remaining mixture (B)

into pure acetic acid and high boilers in an acetic acid

distillation column, and conveying the mixture (A) to a phase

separator (25) from which the resulting aqueous phase

containing residual solvent is recirculated to the solvent

stripping column (11) and the organic phase is recirculated

to the extractor (7).

In the first step (extraction) of the process of the
invention (Fig. 1), the crude acid feed comprising varying
proportions of acetic acid, formic acid, water and high
boilers is fed via a line (6) to an extractor (7) and brought
into contact with a solvent. The extractor (7) can have a
single-stage or preferably multistage configuration. The
solvent stream can, in this process, be directed in the
direction of flow of the crude acid or preferably be conveyed
in countercurrent to the crude acid. Solvents which can be
used here are ethers, esters, ketones, alcohols, saturated,
unsaturated and cyclic hydrocarbons having from 4 to 8 carbon
atoms and their mixtures, preferably ethers and esters having
from 4 to 7 carbon atoms, particularly preferably methyl
tert-butyl ether, diisopropyl ether, di-n-propyl ether, ethyl
butyl ether, ethyl acetate and isopropyl acetate, in a mixing
ratio to crude acid (volume/volume) of from 0.5 to 20,
preferably from 1 to 5, particularly preferably from 1.5 to
3.5 (ratio volume/volume). The extraction can take place in a
temperature and pressure range in which the extraction
solvent and the crude acid are present in liquid form and as
separate phases, i.e. with a miscibility gap. Preference is
given to a temperature range from 0°C to 60°C and a pressure
range from $1*10^5$ to $20*10^5$ Pa.

The raffinate obtained from the extractor (7) is fed
via line (15) to the solvent stripping column (11) where pure

water is taken off at the bottom (line (13)). The product from the top of the solvent stripping column is fed to a phase separator (9). The aqueous phase obtained there goes via line (10) back to the top of the solvent stripping column (11), while the organic phase obtained is recirculated via line (14) to the extractor (7).

The extract taken off from the extractor (7), comprising varying proportions of solvent, acetic acid, formic acid, water and high boilers, is conveyed from the extractor to a solvent distillation column (8).

The solvent distillation column (8) can be operated under atmospheric pressure, but preferably under superatmospheric pressure.

The solvent distillation column (8) is preferably operated under a pressure of $1*10^5$ to $50*10^5$ Pa, preferably from $1*10^5$ to $25*10^5$ Pa, particularly preferably from $1*10^5$ to $5*10^5$ Pa.

In this column, the extract is divided into two substreams by distillation. One substream (mixture (A)), comprising a mixture of solvent and water, is taken off at the top of the column and fed to a phase separator (25) (line (24)). The aqueous phase containing residual solvent is separated off via line (26), and fed to the solvent stripping column (11), preferably at the feed point of the raffinate. The organic

phase is taken off via line (27) and recirculated to the extractor (7).

The second substream (mixture (B)) obtained from column (8), comprising the components acetic acid, formic acid and high boilers, is taken off at the bottom of the solvent distillation column (8) and introduced into an intermediate distillation column (29) (line 28)). The column (29) is likewise operated under atmospheric pressure, but preferably under superatmospheric pressure of from $1*10^5$ to $50*10^5$ Pa, more preferably from $1*10^5$ to $25*10^5$ Pa, particularly preferably from $1*10^5$ to $5*10^5$ Pa. From this column (29), the pure formic acid is taken off at the top via line (19). A mixture of acetic acid and high boilers which is free of formic acid is taken off at the bottom and conveyed via line (31) to an acetic acid distillation column (5) in which the remaining stream is fractionated into pure acetic acid and high boilers. The acetic acid is taken off at the top via line (17) and the high boilers are separated off at the bottom of the column via line (18).

In a particular embodiment (Fig. 2) of the process of the invention, the solvent distillation column (8) is operated in such a way that part of the water is also carried out at the bottom via line (28) and is conveyed together with the acetic acid, the formic acid and the high boilers to the intermediate distillation column (29). In this case, the

water containing small amounts of acetic acid and formic acid is taken off from the distillation column (29) via an additional side offtake and line (35) and is discarded or recirculated via line (35) to the crude acid inlet (6) or another point on the extractor (7).

In this embodiment, the separation function in the solvent column (8) is significantly simplified compared to the process shown in Fig. 1 by the codischarge of water. Furthermore, the additional side offtake on the formic acid distillation column (29) also simplifies the separation into pure formic acid and the bottom product comprising acetic acid and high boilers.

In a further embodiment (Fig. 3) of the process of the invention, the solvent distillation column (8) is likewise operated in such a way that the substream (mixture (B)) separated off at the bottom via line (28) still contains small amounts of water in order to make the separation easier.

This bottom product, comprising acetic acid, formic acid and small amounts of water, is fractionated in an intermediate distillation column (29) into a bottom product which comprises acetic acid and high boilers and is free of formic acid and a mixed top product comprising formic acid, water and small amounts of acetic acid.

The product from the top of the distillation column (29), comprising formic acid, water and small amounts of acetic acid, is subsequently conveyed via line (19) to the pure formic acid distillation column (33). This column (33) is operated at a lower pressure than the intermediate distillation column (29). The pressure difference between column (33) and column (29) is from $0.1*10^5$ Pa to $25*10^5$ Pa, preferably from $0.5*10^5$ Pa to $5*10^5$ Pa. In the pure formic acid distillation column (33), the product stream is fractionated into pure formic acid via line (34) as top product and a mixed bottom product comprising acetic acid, formic acid and water. This bottom product is recirculated via line (32) to the extract stream or another feed point on the solvent distillation column (8).

The raffinate stream (15) from the extractor (7) and the aqueous phase (26) from the phase separation vessel (25) are conveyed to the solvent stripping column (11). Pure water is taken off at the bottom of this column via line (13). The product from the top of this column is conveyed to the phase separator (9). The organic phase obtained is recirculated to the extractor (7), and the aqueous phase is fed into the top of the stripper column (11) via line (10).

In this process variant, it is of great advantage that the demands made of the separation efficiency of the separation column (29) are significantly reduced by the

additional pure formic acid distillation (33) under lower
pressure than in the separation column (29). This results in
a significant energy saving together with greatly improved
formic acid purity compared with comparable processes.
Furthermore, the heat of condensation of the distillation
column (29) can be used in an integrated heat system for
heating the formic acid distillation column (33) and the
solvent column (11). The heat of reaction of the reactions
preceding this separation process, for example a catalytic
gas-phase oxidation of hydrocarbons, can likewise be used for
heating the solvent distillation column (8), the distillation
column (29), the formic acid distillation column (33) and the
acetic acid distillation column (5).

The following examples illustrate the process of the
invention with reference to the figures:

Example 1:

In an apparatus corresponding to the embodiment of
Fig. 3, a crude acid stream comprising 12.9 kg/h of acetic
acid, 2.6 kg/h of formic acid, 48.4 kg/h of water and
0.8 kg/h of high boilers was fed via line (6) to the
extractor (7) (countercurrent extraction column with
stationary stainless steel packing, organic phase dispersed).
Via line (27) and line (14), a solvent return stream
containing 135.4 kg/h of methyl tert-butyl ether (MTBE),

4.0 kg/h of water, 0.5 kg/h of acetic acid and 0.2 kg/h of formic acid was fed to the extractor (7) in the steady state. The extract stream leaving the extractor (7) was composed of 133.9 kg/h of MTBE, 13.1 kg/h of acetic acid, 8.1 kg/h of water, 2.6 kg/h of formic acid and 0.1 kg/h of high boilers. The raffinate stream leaving the extractor (7) via line (15) was composed of 44.7 kg/h of water, 1.5 kg/h of MTBE, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and 0.7 kg/h of high boilers.

The solvent distillation column (8) and the distillation column (29) were operated at a pressure of 2.75 * 10^5 Pa. The pure formic acid column (33) and the pure acetic acid column (5) were operated at a pressure of 1*10^5 Pa.

At the bottom of the solvent column (8), a stream comprising 13.4 kg/h of acetic acid, 3.7 kg/h of formic acid, 0.2 kg/h of water and 0.1 kg/h of high boilers was taken off at a temperature of 147°C via line (28). From the phase separator (25), which was connected to the top of column (8) via line (24), an organic phase comprising 133.8 kg/h of MTBE, 0.5 kg/h of acetic acid, 0.2 kg/h of formic acid and 4.1 kg/h of water was recirculated via line (27) to the solvent inlet of the extractor (7). The stream of aqueous phase leaving the phase separator via line (26) was composed

of 0.03 kg/h of acetic acid, 0.01 kg/h of formic acid,
4.1 kg/h of water and 0.1 kg/h of MTBE.

At the bottom of the distillation column (29), a
stream comprising 12.6 kg/h of acetic acid and 0.1 kg/h of
high boilers was taken off at a temperature of 154.1°C via
line (31). At the bottom of the pure acetic acid column (5),
a stream comprising 0.06 kg/h of acetic acid and 0.1 kg/h of
high boilers was taken off at a temperature of 143.6°C via
line (18).

The stream leaving the top of the pure formic acid
column (33) via line (34) comprised 2.4 kg/h of formic acid.
From the bottom of the pure formic acid column (33), a stream
comprising 0.8 kg/h of acetic acid, 1.3 kg/h of formic acid
and 0.2 kg/h of water was taken off at a temperature of
106.2°C and recirculated via line (32) to the inlet of the
solvent distillation column (8).

The aqueous stream leaving the bottom of the solvent
stripping column (11) via line (13) comprised 48.4 kg/h of
water, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and
0.7 kg/h of high boilers. The return stream of organic phase
via line (14) from the phase separation vessel (9) of the
solvent stripper (11) to the solvent inlet of the extractor
(7) was composed of 1.6 kg/h of MTBE, 0.01 kg/h of acetic
acid, 0.01 kg/h of formic acid and 0.05 kg/h of water.

Fractionation of the crude acid mixture into 2.4 kg/h of 99.9% purity by weight formic acid, 12.5 kg/h of 99.9% purity by weight acetic acid and 49.6 kg/h of 97.5% purity by weight water required, without preheating of the feed upstream of the distillation columns, the following energy input:

bottom heating of the solvent distillation column (8): 20.5 kW

bottom heating of the separation column (29): 10 kW

bottom heating of the pure formic acid column (33): 5 kW

bottom heating of the pure acetic acid column (5): 3.4 kW

bottom heating of the solvent stripping column (11): 4 kW

The total of 43 kW corresponds to 2.87 kW per kg of acid.

Example 2:

In an apparatus corresponding to the embodiment shown in Fig. 3, a crude acid stream comprising 12.9 kg/h of acetic acid, 2.6 kg/h of formic acid, 48.4 kg/h of water and 0.8 kg/h of high boilers was fed via line (6) to the extractor (7) (countercurrent extraction column with stationary stainless steel packing, organic phase dispersed). A solvent return stream comprising 135.4 kg/h of methyl tert-butyl ether (MTBE), 4.0 kg/h of water, 0.5 kg/h of acetic acid and 0.2 kg/h of formic acid was fed to the extractor (7) via line (27) and line (14). The extract stream leaving the

extractor (7) was composed of 133.9 kg/h of MTBE, 13.1 kg/h
of acetic acid, 8.1 kg/h of water, 2.6 kg/h of formic acid
and 0.1 kg/h of high boilers. The raffinate stream leaving
the extractor (7) via line (15) was composed of 44.6 kg/h of
water, 1.5 kg/h of MTBE, 0.4 kg/h of acetic acid, 0.2 kg/h of
formic acid and 0.7 kg/h of high boilers.

The solvent distillation column (8) and the
distillation column (29) were operated at a pressure of
$1.0*10^5$ Pa. The pure formic acid column (33) was operated at
a pressure of $0.25*10^5$ Pa. The pure acetic acid column (5)
was operated at a pressure of $1*10^5$ Pa.

At the bottom of the solvent column (8), a stream
comprising 13.4 kg/h of acetic acid, 3.7 kg/h of formic acid,
0.2 kg/h of water and 0.1 kg/h of high boilers was discharged
at a temperature of 110°C via line (28). From the phase
separator (25), which was connected to the top of the column
(8) via line (24), an organic phase comprising 133.8 kg/h of
MTBE, 0.5 kg/h of acetic acid, 0.2 kg/h of formic acid and
4.0 kg/h of water was recirculated via line (27) to the
solvent inlet of the extractor (7). The stream of aqueous
phase leaving the phase separator via line (26) was composed
of 0.03 kg/h of acetic acid, 0.01 kg/h of formic acid,
4.0 kg/h of water and 0.1 kg/h of MTBE.

At the bottom of the distillation column (29), a
stream comprising 12.6 kg/h of acetic acid and 0.1 kg/h of

high boilers was taken off at a temperature of 117.8°C via line (31). At the bottom of the pure acetic acid column (5), a stream comprising 0.1 kg/h of acetic acid and 0.1 kg/h of high boilers was taken off at a temperature of 143.6°C via line (18).

The stream leaving the top of the pure formic acid column (33) via line (34) comprised 2.4 kg/h of formic acid. A stream comprising 0.8 kg/h of acetic acid, 1.3 kg/h of formic acid and 0.2 kg/h of water was taken off at the bottom of the pure formic acid column (33) at a temperature of 68.6°C and recirculated via line (32) to the inlet of the solvent distillation column (8).

The aqueous stream leaving the bottom of the solvent stripper column (11) via line (13) comprised 48.4 kg/h of water, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and 0.7 kg/h of high boilers. The return stream of organic phase via line (14) from the phase separation vessel (9) of the solvent stripper (11) to the solvent inlet of the extractor (7) was composed of 1.6 kg/h of MTBE, 0.01 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.01 kg/h of water.

Fractionation of the crude acid mixture into 2.4 kg/h of 99.9% purity by weight formic acid, 12.5 kg/h of 99.9% purity by weight acetic acid and 49.6 kg/h of 97.5% purity by weight water required, without preheating of the feed

upstream of the distillation columns, the following energy

input:

bottom heating of the solvent distillation column (8): 30 kW

bottom heating of the separation column (29): 18 kW

bottom heating of the pure formic acid column (33): 3 kW

bottom heating of the pure acetic acid column (5): 5 kW

bottom heating of the solvent stripping column (11): 4.5 kW

The total of 60.5 kW corresponds to 4.05 kW per kg of acid.

Example 3:

In an apparatus corresponding to the variant shown in

Fig. 2, a crude acid stream comprising 12.8 kg/h of acetic

acid, 2.5 kg/h of formic acid, 48.6 kg/h of water and

0.8 kg/h of high boilers was fed via line (6) to the

extractor (7) (countercurrent extraction column with

stationary stainless steel packing, organic phase dispersed).

A solvent return stream comprising 179.7 kg/h of methyl tert-

butyl ether (MTBE), 1.9 kg/h of water, 0.4 kg/h of acetic

acid and 0.1 kg/h of formic acid was fed to the extractor (7)

via line (27) and line (14). The extract stream leaving the

extractor (7) was composed of 178.3 kg/h of MTBE, 13.1 kg/h

of acetic acid, 9.8 kg/h of water, 2.6 kg/h of formic acid

and 0.2 kg/h of high boilers. The raffinate stream leaving

the extractor (7) via line (15) was composed of 40.7 kg/h of

water, 1.3 kg/h of MTBE, 0.2 kg/h of acetic acid, 0.1 kg/h of formic acid and 0.6 kg/h of high boilers.

The solvent distillation column (8) and the distillation column (29) were operated at a pressure of $2.75*10^5$ Pa. The pure acetic acid column (5) was operated at a pressure of $1*10^5$ Pa.

At the bottom of the solvent column (8), a stream comprising 12.6 kg/h of acetic acid, 2.4 kg/h of formic acid, 0.1 kg/h of water and 0.2 kg/h of high boilers was discharged at a temperature of 148.7°C via line (28). The substream separated off at the top via line (24) was fed to the phase separator (25) and separated there. The organic phase obtained, comprising 177.9 kg/h of MTBE, 0.4 kg/h of acetic acid, 0.1 kg/h of formic acid and 1.8 kg/h of water, was recirculated to the extractor (7) via line (27). The stream of aqueous phase leaving the separator via line (26) was composed of 0.03 kg/h of acetic acid, 0.02 kg/h of formic acid, 7.8 kg/h of water and 0.4 kg/h of MTBE.

At the bottom of the distillation column (29), a stream comprising 12.5 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.1 kg/h of high boilers was taken off at a temperature of 154.2°C via line (31). At the bottom of the pure acetic acid column (5), a stream comprising 0.04 kg/h of acetic acid and 0.1 kg/h of high boilers was taken off at a temperature of 150°C via line (18).

The stream leaving the top of the distillation column (29) via line (19) comprised 0.01 kg/h of acetic acid, 2.4 kg/h of formic acid and 0.01 kg/h of water. A side offtake stream comprising 0.05 kg/h of acetic acid, 0.8 kg/h of formic acid and 0.1 kg/h of water was taken from the column (29) via line (35).

The aqueous stream leaving the bottom of the solvent stripping column (11) via line (13) comprised 48.5 kg/h of water, 0.3 kg/h of acetic acid, 0.08 kg/h of formic acid and 0.6 kg/h of high boilers. The return stream of organic phase to the extractor via line (14) from the phase separation vessel (9) of the solvent stripper (11) was composed of 1.7 kg/h of MTBE, 0.01 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.05 kg/h of water.

Fractionation of the crude acid mixture into 1.6 kg/h of 98.6% purity by weight formic acid, 12.5 kg/h of 99.99% purity by weight acetic acid and 49.4 kg/h of 98.1% purity by weight water required, without preheating of the feed upstream of the distillation columns, the following energy input:

bottom heating of the solvent distillation column (8): 22.5 kW

bottom heating of the separation column (29): 10 kW

bottom heating of the pure acetic acid column (5): 4 kW

bottom heating of the solvent stripping column (11): 4.5 kW

The total of 41 kW corresponds to 2.9 kW per kg of acid.